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MOLECULAR ENERGY TRANSFER BY COLLISIONAL PROCESSES CHARACTERIST--ETC(U)
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PROCESSES CHARACTERISTIC OF GAS LASERS

NEVADA UNIVERSITY, RENO, NEVADA

1 JANUARY 1977

AEOSR - TR - 77 - 0001

DEC 15 1976

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FINAL REPORT

January 1, 1977

PROJECT TITLE: "Molecular Energy Transfer by Collisional Processes
Characteristic of Gas Lasers"

GRANT NUMBER: AFOSR-72-2231

TO: Directorate of Chemical Sciences
Air Force Office of Scientific Research
Department of the Air Force
Bolling AFB, Bldg. 410
Washington, D. C. 20332

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 77 - 0001	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) MOLECULAR ENERGY TRANSFER BY COLLISIONAL PROCESSES CHARACTERISTIC OF GAS LASERS		5. TYPE OF REPORT & PERIOD COVERED Final; Jan. 1, 1972 - Dec. 31, 1976
7. AUTHOR(s) Hyung Kyu Shin		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Nevada Reno, Nevada 89507		8. CONTRACT OR GRANT NUMBER(s) AFOSR-72-2231
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research/NC Bolling AFB, Bldg. 410 Washington, DC 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F, 681303, 9538-01
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 1977
		13. NUMBER OF PAGES 11
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Transition probability Vibrational energy transfer Chemical laser Self-relaxation (continued on reverse side)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The major objective of this project was to develop theoretical models for the calculation of transition probabilities in collisions of atoms and molecules. New methods have been developed, and existing techniques have been refined to provide both a quantitative and a qualitative interpretation of the mechanisms and dynamics of molecular collisions. Special emphasis is given to the problem of deriving explicit expressions for energy transfer probabilities, so their dependence on pertinent collision parameters can be readily determined. (continued on reverse side)		

Continued

(19) Key words:

Hydrogen-bond interaction
Dipole-dipole interaction
Negative temperature dependence
Vibration-rotation energy transfer
Isotope effect
Rate coefficient
Reaction cross section
Positive energy dependence
Impulsive collision
Number of impacts
Sudden approximation
Interference effect
Translational nonequilibrium
Collision-induced light scattering
WKB evaluation

(20) Abstract:

Whenever possible, the theoretical study has been tested against experimental data, not only for demonstrating the utility of the theoretical formulation for the prediction and correlation of experimental results, but also for explaining the observations and using the discrepancies between theory and experiment to further refine our understanding of energy transfer processes. The most important investigation carried out during the tenure of this grant has dealt with the vibrational energy transfer processes in hydrogen fluoride molecules, which play major roles in chemical laser operation. In this investigation, we have considered the self-relaxation of $\text{HF}(1)/\text{DF}(1)$, near-resonant vibration-vibration energy transfer processes in $\text{HF}(n) + \text{HF}(0)$ and $\text{DF}(n) + \text{DF}(0)$, vibrational energy transfer in $\text{CO}_2(00^01) + \text{HF/DF}$, and F-atom deexcitation of HF/DF . In addition, the following aspects of molecular collisions have also been investigated: vibration-rotation energy transfer in H_2O and NH_3 , near-resonant vibration-vibration energy transfer in $\text{N}_2 + \text{CO}$, intramolecular vibration-rotation energy transfer in $\text{HF} + \text{Ar}$, simultaneous vibrational and rotational transitions in $\text{H}_2 + \text{Ar}$, semiclassical approach to vibrational energy transfer in $\text{H}_2 + \text{He}$, and translational energy dependence of the reaction cross sections of alkali-methyl iodide reactions.

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1. TITLE: "Molecular Energy Transfer by Collisional Processes
Characteristic of Gas Lasers"
2. PRINCIPAL INVESTIGATOR: Hyung Kyu Shin, Professor
Department of Chemistry
University of Nevada
Reno, Nevada 89507
3. INCLUSIVE DATES: 1 January 1972 - 31 December 1976
4. GRANT NUMBER: AFOSR-72-2231
5. COSTS: \$127,290*
6. SENIOR RESEARCH PERSONNEL: (Visiting Professors)
Dr. Y. H. Kim
Dr. J. Keizer
7. JUNIOR RESEARCH PERSONNEL: A. W. Young
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* Approximately \$30,000 will be reverted.

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List of Publications

- *1. H. K. Shin, "Excitation of Molecular Vibration on Collision. Simultaneous Vibrational and Rotational Transitions in $\text{H}_2 + \text{Ar}$ at High Collision Velocities," J. Phys. Chem., 76, 2006 (1972).
- *2. H. K. Shin, "Temperature Dependence of Vibrational Transition Probabilities for O_2 , N_2 , CO , and Cl_2 in the Region Below 300°K ," J. Chem. Phys., 57, 3484 (1972).
- *3. H. K. Shin, "Temperature Dependence of the Probability of Vibrational Energy Transfer Between HF and F ," Chem. Phys. Letters, 14, 64 (1972).
- *4. H. K. Shin, "De-excitation of $\text{CO}_2(00^01)$ by Hydrogen Fluorides," J. Chem. Phys. 57, 3484 (1972).
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* Reprints already submitted to AFOSR

ABSTRACT

The major objective of this project was to develop theoretical models for the calculation of transition probabilities in collisions of atoms and molecules. New methods have been developed, and existing techniques have been refined to provide both a quantitative and a qualitative interpretation of the mechanisms and dynamics of molecular collisions. Special emphasis is given to the problem of deriving explicit expressions for energy transfer probabilities, so their dependence on pertinent collision parameters can be readily determined. Whenever possible, the theoretical study has been tested against experimental data, not only for demonstrating the utility of the theoretical formulation for the prediction and correlation of experimental results, but also for explaining the observations and using the discrepancies between theory and experiment to further refine our understanding of energy transfer processes. The most important investigation carried out during the tenure of this grant has dealt with the vibrational energy transfer processes in hydrogen fluoride molecules, which play major roles in chemical laser operation. In this investigation, we have considered the self-relaxation of HF(1)/DF(1), near-resonant vibration-vibration energy transfer processes in HF(n) + HF(0) and DF(n) + DF(0), vibrational energy transfer in CO₂(00°1) + HF/DF, and F-atom deexcitation of HF/DF. In addition, the following aspects of molecular collisions have also been investigated: vibration-rotation energy transfer in H₂O and NH₃, near-resonant vibration-vibration energy transfer in N₂ + CO, intramolecular vibration-rotation energy transfer in HF + Ar, simultaneous vibrational and rotational transitions in H₂ + Ar, semiclassical approach to vibrational energy transfer in H₂ + He, and translational energy dependence of the reaction cross sections of alkali-methyl iodide reactions.

COMPLETED PROJECT SUMMARY

Our major activity under this grant has been the study of the vibrational energy transfer in hydrogen fluoride molecules. One of the systems we have investigated is the self-relaxation of hydrogen fluorides over wide temperature ranges. Vibrational relaxation times of HF have been calculated on the basis of the vibration-rotation energy transfer theory over the temperature range 300 - 4000°K. We have shown that the vibrational relaxation of hydrogen fluoride molecules can be rigorously explained in terms of the model of vibration-to-rotation energy transfer when the effects of dipole-dipole and hydrogen-bond interactions are included. Statistically the colliding molecules spend more time in those orientations for which the dipole-dipole and hydrogen-bond attractions are large, thus causing the molecules to exchange their energies efficiently. Below 1000°K, the relaxation time becomes very short showing a strong negative temperature dependence, which can be attributed to the contributions of such attractive forces. Over the entire temperature range, the agreement between calculation based on the vibration-rotation energy transfer theory and experimental data in both the magnitude and temperature dependence of vibrational relaxation time is found to be good.

At temperatures below 300°K, the contribution of hydrogen-bond attraction becomes important. Because of this contribution, the colliding molecules can form a nonrigid bond and undergo oscillatory motion about their equilibrium orientations. Such sticky collisions are shown to be primarily responsible for the removal of the vibrational energy of HF(1) and lead to a negative temperature dependence of energy transfer probability. The model has been extended to study near-resonant collisions $\text{HF}(n) + \text{HF}(0) \rightarrow \text{HF}(n-1) + \text{HF}(1)$ and $\text{DF}(n) + \text{DF}(0) \rightarrow \text{DF}(n-1) + \text{DF}(1)$ for $n = 2 - 5$ in the temperature range 200 - 2000°K. We have shown that the formation of a nonrigid hydrogen bond is important at lower

temperatures, while the complete rotational motion is responsible for the removal of vibrational energy at higher temperatures. For the latter case, the vibration-rotation energy transfer mechanism has been used. At a given temperature the sum of these two contributions determines the efficiency of near-resonant vibrational energy transfer processes. The rate coefficient k for $\text{HF}(n) + \text{HF}(0) \rightarrow \text{HF}(n-1) + \text{HF}(1)$, where $n = 2$ and 3 , shows a strong negative temperature dependence at low temperatures where the nonrigid dimer mechanism is of primary importance; after reaching a minimum value it then increases with rising temperature. For $n = 5$, no such dependence is found. At higher temperatures the rotational motion of HF is primarily responsible for the removal of energy mismatch. Another interesting result found is that at low temperatures the rate coefficient decreases with n , but it increases at higher temperatures. These two different n -dependent regions are separated approximately at 300°K ; at this temperature, k for $n = 3$ is shown to be the largest. In the neighborhood of room temperature, the dependence of k on n is very sensitive to a small change in temperature. The maximum k occurs at either $n = 3$ or 4 , but near 400°K , k can even be an increasing function of n . For DF systems, however, k always increases with n over the temperature range $200 - 2000^\circ\text{K}$, although the increase is much smaller at lower temperatures. The hydrogen-bond interaction model has also been used in the study of $\text{HF}(1) + \text{H}_2\text{O}(000) \rightarrow \text{HF}(0) + \text{H}_2\text{O}(001)$ in the temperature range $300 - 500^\circ\text{K}$.

Another important study involving hydrogen fluorides carried out under the support is the F-atom deexcitation of $\text{HF}(1)/\text{DF}(1)$. We have developed a rigorous semiclassical approach to determine deexcitation rate coefficients of these collisions with special emphasis on the temperature dependence of rate coefficients and isotope effect. Near room temperature, k of $\text{HF}(1) + \text{F} \rightarrow \text{HF}(0) + \text{F}$ is small but it rapidly increases with temperature. At temperatures above 1500°K , k is

very large with the magnitude $10^{13} \text{ cm}^3/\text{mole-sec}$. We have found that $\text{DF}(1)$ relaxes two to three times faster than $\text{HF}(1)$ in the range $100^\circ - 3000^\circ\text{K}$.

We have also studied the energy transfer in $\text{CO}_2 + \text{HF/DF}$ in the temperature range $300 - 2000^\circ\text{K}$. The calculation based on the vibration-rotation energy transfer theory shows the efficient deexcitation of $\text{CO}_2(00^1)$. The calculated values are in agreement with laser-excited fluorescence measurements around 350°K . From a comparison with experimental data it is predicted that the (final) deexcited states of CO_2 are (00^0) and (01^1) , respectively, for the $\text{CO}_2(00^1) + \text{HF}$ and $\text{CO}_2(00^1) + \text{DF}$ collisions. The vibration-rotation theory was used to study the temperature dependence of the near-resonant process $\text{HCl}(2) + \text{HCl}(0) \rightarrow \text{HCl}(1) + \text{HCl}(1)$. Since the hydrogen-bond interaction is weak in these molecules, the dimer model was not considered for this process. Extension of the energy transfer theory has been made to other polar molecules such as H_2O and NH_3 over wide temperature ranges. Calculations show that deexcitation probabilities are large in these collisions, and furthermore, D_2O is shown to be less efficiently deexcited than H_2O in the self-deexcitation processes.

Another area of research has been the development of an impulsive collision model to study the translational energy dependence of the reaction cross section of all the alkali-methyl iodide reactions, the reactions which have been extensively investigated by molecular-beam kineticists. For $\text{CH}_3\text{I} + \text{K} \rightarrow \text{CH}_3 + \text{KI}$ the model gives reaction cross sections which are in good agreement with experimental data in the pre- and post-maximum energy regions. In all reactions of the family, the cross section increases sharply with the translational energy showing an Arrhenius-like positive energy dependence for the energy just past threshold and then takes a maximum value. In the post-maximum region the cross section decreases slowly with the translational energy.

The impulsive collision model has been extended to study the dependence of vibration-translation energy exchange in nonreactive collisions on the number of impacts. For the collinear collision C-B + A, the total number of impacts that a single collision can have is $n = 90^\circ/\phi$, where $\phi = \arctan [m_B(m_A+m_B+m_C)/m_A m_B]^{1/2}$; for nonintegral values of $90^\circ/\phi$, n is the interger which just exceeds the noninteger value $90^\circ/\phi$. The model is applied to H-F + F, F-H + F, Cl-H + Cl, Br-H + Br, I-H + Cl, and several other hypothetical systems with particular emphasis on the dependence of energy exchange on the number of impacts. Comparison with exact trajectory calculations at high collision energies shows a diminished inelasticity as the result of repeated impacts between A and B in a single collision.

A rigorous semiclassical approach has been developed to study vibrational energy transfer in $H_2 + He$ by use of the a priori interaction potential including all nonzero impact parameter collisions. The calculated values of the rate coefficient are found to be in excellent agreement with experimental data which are available in the temperature ranges $60^\circ - 450^\circ K$ and $1350^\circ - 3000^\circ K$.

We have also investigated the following problems in molecular collisions. The importance of rotational transitions in the vibrational deexcitation of HF(1) in HF + Ar collisions has been studied by a semiclassical three-dimensional approach. The temperature dependence of intramolecular vibrational energy transfer in $CO_2(00^01) + Ne/CO_2 + CO_2(nm^00) + Ne/CO_2$ has been investigated. An analytic approach has been developed to study vibration-vibration energy transfer in near-resonant collisions; the model has been applied to Cl + M, where M = N_2 , NO, O_2 , and D_2 . The 0 + 1 vibrational transition probability of an anharmonic oscillator has been formulated using the potential function which is a sum of quadratic and cubic terms in the vibrational coordinate. The problem of vibrationally and rotationally inelastic scattering processes in $H_2 + Ar$ for nonzero

impact parameter has been investigated in the collision velocity range $10^6 - 10^7$ cm/sec by use of the sudden approximation. The interference between one- and two-quantum excitation processes in $0 \rightarrow n$ vibrational transitions taking place in molecular collisions has been investigated. A rigorous comparison of the WKB evaluation of the quantal approach to vibrational energy transfer with the purely classical theory has been carried out. The temperature dependence of vibrational energy transfer for O_2 , N_2 , CO and Cl_2 at temperatures below $300^\circ K$ has been investigated. Interference effects in the collision of a molecule with two incident particles have been investigated using the classical approach to vibrational energy transfer. Also investigated are translational nonequilibrium during vibrational relaxation and collision-induced light scattering.